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Cost-Effective Emission Management and Ventilation of Large Aircraft Painting Facilities: Oxidation of Toluene and of MEK Adsorbed to Irradiated Hopcalite

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13. ABSTRACT *(Maximum 200 words)* In many AF aircraft painting operations the use (and cost to use) ventilation air is excessive. Reluctance to recirculate filtered ventilation air, coupled with overcompliance with ventilation rate standards in 29 CFR 1910.94(c)(6)(ii) exaggerates energy costs by as much as a factor of 10; for low-observable coatings, the savings in HVAC costs can be significant. Further, treatment to remove contaminants in the recirculating circuit is not an exhaust emission treatment, so such treatment should comprise a source-reduction strategy. In 1992 Seymour Johnson AFB, North Carolina, applied these concepts in designing a recirculating hangar whose process for decontamination of the recirculated air was base on an alleged room-temperature catalyst, hopcalite that had earlier been exposed to e-beam radiation. After a year in service, samples of recovered catalyst were found to exhibit no discriminable activity in room-temperature tests at EPA and at AFRL, but heating of a solvent-saturated sample produced rapid oxidation at ~190°C. Extrapolation of the estimated half-life for reaction at 190°C to 20°C predicted a half-life for reaction of the solvent in days, which created a possibility that oxidative recovery occurs too slowly to observe easily. Long-term tests with toluene and MEK are described, and the experimental results of these tests eliminate the possibility of such a slow recovery process, indicating that the "activation" treatment afforded no more than temporary enhancement (continued on p. ii)

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of catalytic activity. However, the failure of the specific control installed does not invalidate the concept of inserting a VOC-removal device into the recirculating ventilation stream as a process element to lower concentrations inside the workspace—or the collateral benefit of reducing the magnitude of the emission source—and further pursuit of such designs is strongly encouraged as an energy-saving measure.

EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of this project was to investigate the possibility that low-temperature oxidation of adsorbed organic vapors is catalyzed by samples of hopcalite previously activated by electron-beam irradiation *in vacuo*.

B. BACKGROUND

When environmental conditions or coating properties require the application of process cooling or heating to ventilation air to be used during spray painting of aircraft, associated costs for energy contribute substantially to the life-cycle cost for that aircraft. Acquisition, operating, and maintenance costs for the ventilation (HVAC) system increase with the volume of air being moved into and out of the facility, which may be lower than the rate of air movement inside the workspace, the work safety parameter that is regulated under 29 CFR 1910.

Whereas the Air Force has traditionally used ~120 ft/min (cfm flow/ft^2 cross sectional area) of fresh air to ventilate its aircraft painting operations, significant economies (particularly in climate-controlled facilities) can be realized by some combination of lowering the flow rate inside the workspace and recirculating a fraction of the exhaust to recover the energy invested to condition that air. Both measures may slightly raise the concentration of airborne air toxics in the workspace, but the extent of this increase is limited by 29 CFR 1910.1000 and 1910.94(c)(6)(ii), which address Permissible Exposure Limits (PELs) and Lower Explosive Limits (LELs), respectively, of airborne contaminants.

Seymour Johnson AFB (SJAFB), N.C., attempted to mitigate both the increment to concentration in the workspace and the net rate of emission of Volatile Organic Compounds (VOCs) to the atmosphere by introducing a room-temperature oxidation catalyst as an element of the air-treatment system in a recirculating hangar used to paint F-15s. The catalyst, a preparation of hopcalite that had been subjected to electron-beam irradiation in a hard vacuum, showed initial activity at room temperature and was apparently not retested later. After a year in service, samples were tested by EPA-AEERL and by this lab, and found to be inactive at room temperature. However, heating a toluene-saturated sample produced lightoff at ~180 °C, which suggested the possibility that the rate of oxidation at room temperature may be finite but extremely slow. This investigation examined that possibility.

C. SCOPE

This report summarizes the results of two master of science theses that examined the long-term behavior of toluene and butanone (MEK), respectively, in contact with freshly heated samples of the hopcalite catalyst recovered from SJAFB.

D. METHODOLOGY

Reactions were conducted in cylindrical glass vessels sealed at both ends by stem valves. A metal cap placed on each end allowed introduction or removal of gases and catalyst pellets, and created isolated volumes of ~ 1 cm^3. A septum and a stop-and-go sliding seal sealed a third port at the top of the vessel. The headspace was sampled through the septum by insertion of a solid-phase microextraction (SPME) tool, which was then retracted and inserted into a gas chromatograph (gc) for rapid desorption and analysis. A gas-tight syringe was inserted through the septum at the end of some experimental periods to collect samples for analysis of CO_2 by gc and a mass-selective detector.

E. TEST DESCRIPTION

Uniform-sized pellets of hopcalite were selected, heated to 100 °C for an hour, and introduced into the end chamber of a glass vessel that had been exhaustively purged with air. The main volume of the vessel was then charged through the opposite port with a measured amount of solvent. After mixing was judged complete, the SPME was used to sample the headspace. At $t = 0$ the pellet was introduced into the main volume by opening the stopcock separating the two chambers and tipping the vessel, and the headspace was sampled at intervals during a period of 10–30 days. A vessel without hopcalite was run concurrently as a control for leakage. At the end of several runs the concentration of CO_2 in the headspace was measured.

F. RESULTS

For both solvents tested, headspace concentrations dropped very rapidly upon introduction of the hopcalite pellet(s). Although the data were somewhat noisy in individual runs, a combined analysis of the toluene experiments at 24 °C showed an average slope of ~0 from the time of initial stabilization until the end of each experiment. Experiments at 24 °C and 38°C with MEK also showed slopes of ~0 after the presumed adsorption process reached equilibrium. Concentrations of CO_2 at the end of the experiments for which they were measured were indistinguishable from background values. Reintroduction of a fresh charge of solvent into a vessel containing a hopcalite pellet resulted in only a slight decrease in the headspace concentration.

G. CONCLUSIONS

The "modified" catalyst appears to be no different from ordinary hopcalite, so any activation effects from electron bombardment were transitory. The initial drop in concentration observed is consistent with the known capacity of hopcalite as an adsorber. However, the failure of this application was caused by material properties and not a design flaw. The concept of introducing a flameless control that either operates at low temperature or that creates a minimal thermal burden on the HVAC system, and that removes organic vapors as they are released into a recirculating air stream remains a valid approach to lowering concentrations in the circulating and exhaust streams from spray painting facilities.

H. RECOMMENDATIONS

Recirculation and ventilation rates of ~40 ft/min are much more economical alternatives to current painting ventilation practices, and they should be implemented widely. Research should continue into such technologies as atmospheric-pressure nonthermal plasma, low-temperature catalysts, and adsorbers that light off at ~100°C, which offer promise of on-the-fly removal and destruction in place inside recirculating ventilation systems. Until these technologies become available for routine use, activated carbon or zeolite adsorbers will be adequate to remove organic vapors from recirculating air streams.

PREFACE

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1.0 INTRODUCTION

Although the surface coating of legacy aircraft addresses numerous functions, including cosmetics, signature and drag, the most important is suppression of corrosion, which is essential to preserve the long-term functional value of the asset. Solvent vapors emitted during the processes of paint application and cure contribute to the net environmental burden of volatile organic compounds (VOCs). Even when so-called low-VOC coatings are employed, the act of spraying aircraft coatings contributes toxic constituents to the atmosphere both inside and outside the painting area.

During the process of spray painting aircraft, ventilation air addresses four categories of operational needs, discussed briefly below:

1. Control temperature and relative humidity in the painting area;
2. Clear overspray particles to maintain coating quality;
3. Suppress fire and explosion hazards by diluting solvent vapors;
4. Clear air toxic vapors and particles from the breathing zone (BZ) of personnel.

1. Control of temperature and relative humidity in the painting area. Suppliers specify a range of environmental conditions within which application of their coatings is expected to produce the best-finished surface. Application of the coating outside this temperature and humidity window may compromise appearance and service lifetime of the coat and/or exaggerate the frequency and extent of touchups required to produce an acceptable coating. In hot climates, high workspace temperatures require extended rest periods to maintain safe core temperatures in workers, which extends job time and labor cost. In both Northern- and Southern-tier bases, treatment of air to maintain prescribed environmental conditions in the painting area is a significant[1] life-cycle cost center.

2. Clearance of overspray particles to maintain coating quality. Coat texture is roughened by deposition of overspray particles on dry or drying surfaces, which creates a second job-defined requirement for effective ventilation. Particularly in hot or cold locations, the balance between cost to provide conditioned air for environmental control and minimum airflow requirements to provide adequate clearance creates an opportunity for process optimization. Both practical experience and studies modeling and measuring aerosol behavior using a manikin in an experimental painting booth suggest[2] that deposition efficiency from the gun is sensitive to flow velocity and that the effect may not be as drastic in homogeneous airflows at 40–75 ft/min.

3. Suppression of fire and explosion hazards by diluting solvent vapors. As it leaves the gun, sprayed paint is a flammable mixture and as the plume drifts downstream it remains flammable until the vapor concentration is diluted to <1%. At first blush it might appear that the fastest possible dilution—*i.e.*, the largest possible airflow—is ideal. However, excessive airflow lowers efficiency of deposition of sprayed paint and raises the heating and cooling load on the ventilation system. It also increases paint consumption, amplifies net rates of VOC emission, and accelerates the loading of filters. Thus, airflow is a significant factor to manage in any attempt to optimize the ventilation process.

Uniform air movement across the entire painting area is also necessary. It produces consistent dilution and clearance at all times during painting. It also prevents the development of pockets of high concentration in stagnant regions, as observed[3] by Carpenter and Poitrast under large aircraft in a downdraft-painting hangar. The standard for safe operation with respect to solvent vapor fire and explosion hazards is defined[4] in NFPA 33 and a number of derivative rules and interpretations[5]. Solvent vapor concentrations shall not exceed 0.25 of the Lower Explosive Limit (LEL). At ventilation rates consistent with acceptable economics for the painting process, this standard is meaningful only if airflow at the exhaust plane is uniform within $\pm$ 15% across the entire area. Alternative standards specifying minimum airflow rates do not relate directly to exhaust concentrations because they may also affect the vapor generation process, and an OSHA opinion[6] has dismissed velocity-based standards.

4. Clearance of air toxic vapors and particles from the breathing zone (BZ) of personnel. Primers contain large quantities (20–30%) of strontium chromate ($SrCrO_4$), which is a respiratory carcinogen, and topcoats form from reactions of sprayed isocyanates, which are strong respiratory sensitizers. Volatile constituents of the solvents are relatively much less toxic, but all of these chemicals are classified as air toxic materials (ATMs). Worker exposure to ATMs is regulated (currently[7]) under 29 CFR 1910.1000, which specifies individual Personal Exposure Limits (PELs) for each ATM present and a limit to the total burden of all ATMs delivered as an eight-hour, time-weighted average measured in the BZ for a nominal five-day work week.

The PELs for $SrCrO_4$ and isocyanates are sufficiently low that administrative and engineering controls are typically insufficient to reduce exposures reliably below the PEL, so personal protective equipment (PPE) is usually required to attain compliance with the exposure standard (and to mitigate the risk of accidental exposure). An optimization may be possible of exposure risk and ventilation rate, consistent with the manikin[2] study's results, and we have proposed an experimental study in an actual aircraft painting operation to look for a job-averaged minimum in the exposure/velocity relationship. Anecdotal reports from large hangars suggest that this may occur near 40 ft/min, which rate would significantly decrease the life-cycle cost to ventilate during aircraft painting. Because clearance and dilution mitigate both explosion/fire hazards and toxic exposure risks, the same considerations apply to both during any cost–benefit analysis.

1.1 Partial Exhaust Recirculation

Under specified conditions of operation and management, NFPA 33 allows[8] partial recirculation[9] of exhaust air. One condition is effective filtration of the returning air, which has the collateral benefit to personal exposure risk that the most-toxic ATMs present during priming and during topcoating, which occur in particles, are thus each decreased by approximately 99% before recirculation. This has the important effect of limiting accumulation of the particulate ATMs (pATMs) so, at 90% recirculation of exhaust, the maximum attainable increase in exposure risk is estimated[10] to be only a few percent. In contrast, volatile ATMs (vATMs) concentrate in inverse proportion to the

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fraction of air exhausted. As the exhaust rate decreases, steady-state limits of vATM concentrations, which are nearly negligible in single-pass ventilation systems (Figure 1), increase hyperbolically in systems that recirculate filtered exhaust air at a constant rate (Figure 2).
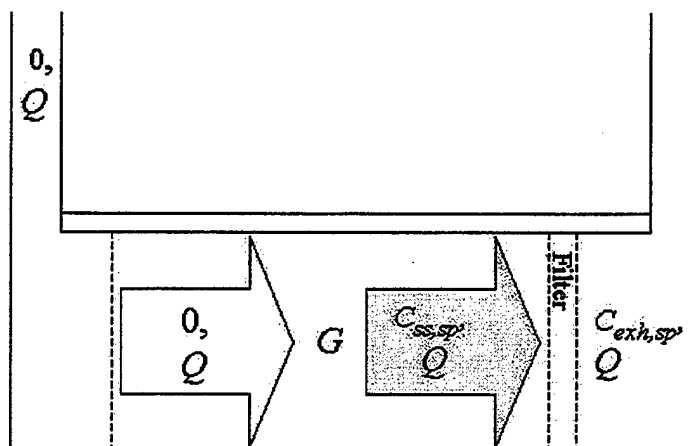

Figure 1. Idealized airflow in a conventional (single-pass) aircraft painting area.

Figure 1 shows the movement of air and ATMs through a ventilated painting enclosure in a horizontal configuration approximating laminar flow. In this hypothetical example of ideal air movement, a nominal single pass of 100,000 cfm of ventilation air, Q, flows through the paint booth's 50-by-20-foot cross section at 100 ± 10 ft/min and is exhausted completely. Movement is nearly uniform at an average of 100 ft/min in the painting area and across the face of the exhaust filters that cover the exhaust plane. During operation, the instantaneous exhaust concentration of vATMs averaged across the exhaust plane, $C_{exh,sp}$ will exponentially approach the steady-state concentration $C_{ss,sp}$ produced by the paint gun(s) operating constantly at maximum delivery rate G,
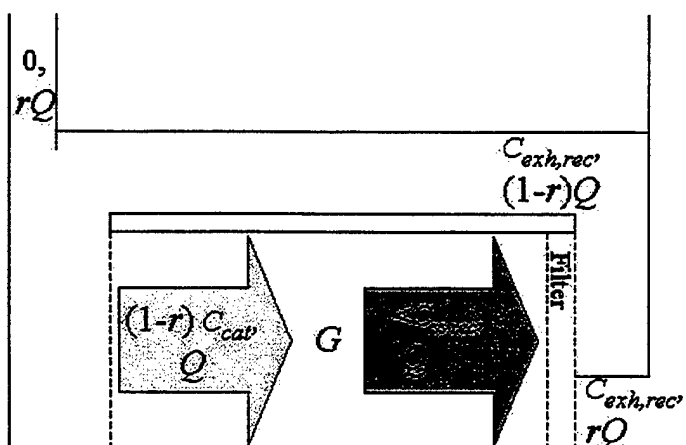
$$C_{exh,sp} < C_{ss,sp} = G/Q$$

Figure 2. Idealized airflow in a recirculating aircraft painting area.

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Continuing the example to Figure 2, in which the exhaust is divided and a fraction rQ is exhausted, the remainder is mixed with fresh air and returned through the painting area (*recirculated*). Here r is defined as the *recirculation ratio* and, for $r = 0.10$, the exhaust rate $rQ = 10,000$ cfm and the remaining 90,000 cfm, comprising 90% of the ventilation stream, is recycled through the added recirculation duct to the intake plenum. To maintain slight negative pressure within the enclosure and thus limit escape of ATMs through leaks, only part of the 10,000 cfm of fresh air makeup is actually introduced through the intake plenum. However, for the purpose of calculating exhaust conditions accuracy will not be significantly be impaired by assuming that the entire volume (rQ) of makeup air enters through the intake plenum.

In comparing the exhaust from a recirculating system to that from a single-pass ventilation system we must recognize that the rate of generation of ATMs by the paint operation (as well as the principal source of toxic exposure risk) remains the same. However, the exhaust after recirculation will include recycled ATMs as well as new ATMs generated from the immediate painting operation. Thus, the concentration of solvent vapors in the recycled exhaust is dependent on both the rate of delivery from the paint gun and the concentration of vATMs in the recycle flow stream, $C_{exh,rec}$. The upper limit of $C_{exh,rec}$ is the steady-state concentration, $C_{ss,rec}$, and a mass balance across the exhaust shows that

$$C_{exh,rec} < C_{ss,rec} = G/rQ = C_{exh,sp}/r$$

For any specific value of r the exhaust solvent vapor concentration will increase from the single-pass-mode value, $C_{exh,sp}$ to[10,11] to a new concentration value, $C_{exh,rec}$. Because G is unaffected, the inlet concentration rises from a nominal 0 to $(1-r)C_{exh,rec}$, for which concentrations a method of estimation[12] is available.

The largest acceptable value for $C_{ss,rec}$ and thus the smallest value for r is governed by safety considerations associated with PELs and LELs. For aircraft paint application at differing values of r, the PELs of the vATMs are several orders of magnitude smaller than PELs for the pATMs, so concentrating vATMs contributes a small increase in exposure risk[12] compared to particulate $SrCrO_4$ in the primer or isocyanates in the topcoat—until r is 0.010 or less. In addition, since the PELs for the vATMs in aircraft paints are so much smaller than their LELs, compliance with the exposure standard ordinarily implies compliance with the fire safety standard.

Recirculation is typically undertaken to decrease the heat load to the heating, ventilating and air conditioning (HVAC) system, which strategy creates cost savings both during installation (smaller heating and cooling components) and during operation (energy consumption is essentially proportional to exhaust rate, because conditioning of recirculated air is retained). Justification[11] for installing a recirculating ventilation system is provided by a cost–benefit analysis of gains realized[1] relative to an operation exhausting 100%.

1.2 Source-Reduction Strategy

Whereas using a device to remove VOCs and particles from the exhaust stream is considered an emission control strategy, placement of a similar device inside the recirculating system creates a different regulatory situation. When such a treatment device operates as part of a recirculation process, the device becomes a process element. Thus, any action that decreases VOC and particle emission rates falls into the category of source reduction rather than exhaust treatment[13]. In addition to source reduction, however, adding this mediation to the recirculation strategy will also oppose the rise in concentration by removing or destroying a significant fraction of the amount of ATMs accumulating in the recirculating air stream. However, this attenuation of the increment to risk is worthwhile only if it can be accomplished without raising the circulating air temperature by more than a few degrees, which requires a device that is effective at or near room temperature.

Granular activated carbon (GAC) is a suitable candidate for thermally neutral decontamination of the recirculating stream, but loading will be rapid and the bed will require either regeneration or replacement at finite intervals to retain activity and to avoid the risk of spontaneous[14] bed fires. Non-thermal plasmas are efficient oxidizers and may eventually have a role in process reduction of VOC concentrations, which is concurrently a reduction of ATM concentrations as well.
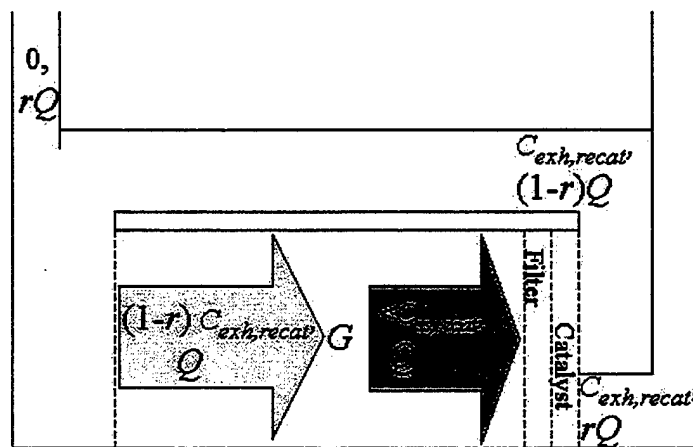

Figure 3. Idealized airflow in a recirculating aircraft painting area with an in-line treatment to remove volatile air-toxic materials (vATMs) from the process.

The concept of on-the-fly oxidation inside the recirculating process loop is another way to accomplish the desired source reduction strategy. This procedure as undertaken by Seymour Johnson AFB (SJAFB) was noted as a very progressive hangar-modification project that received an award for environmental innovation in 1993. SJAFB's decontamination strategy was based on the use of hopcalite, commercially activated by electron-beam irradiation, as a catalyst.

Hopcalite is a mixed oxide of Cu and Mn developed[15] around 1920 by the Navy to oxidize carbon monoxide, CO, in breathing air. Activation was accomplished by electric beam irradiation *in vacuo*. Since a freshly prepared specimen had been shown to be at least briefly reactive at room temperature, the presumption behind the facility design was that oxidation will proceed whenever contaminated air passes through an activated hopcalite bed. Despite this expectation, EPA-AEERL personnel noted no evidence of heat release from the process. Since effective low-temperature oxidation catalysts are rare and tend to be very short-lived, the expectation of long-term performance by hopcalite was speculative. Eventual investigation of samples of aged irradiated hopcalite from the control system by both EPA-AEERL[16] and this laboratory[17] confirmed no detectable evolution of CO_2 during approximately one hour at room temperature.

The generic process illustrated in the SJ facility has been modeled (Appendix) to predict the amount of VOC exhausted as a function of the rate of oxidation (by a catalyst, plasma, or other device) of organic volatiles. Extent of removal can also be a factor for optimization in a cost-as-an-independent-variable calculation. The model is arbitrarily configured to predict the smallest destruction rate constant that will comply with the regulatory requirement[13] for 81% removal and destruction by emission control treatments, but can easily be modified to support design calculations.

As a coda to the investigation of SJAFB's catalyst, this lab also subjected a charge of the recovered catalyst that had been saturated with toluene vapor to ballistic heating and observed abrupt lightoff at approximately190°C, as shown by sudden, rapid condensation of water in a cold region downstream of the catalyst. One interpretation of the set of observations—which included no reports of exceeding PELs during operation—is that the removal mechanism is adsorption of VOCs onto the surface of the hopcalite, which subsequently effects oxidation gradually during the time intervening between paint jobs, typically one to two weeks.

As an example, an oxidation reaction whose half-life is three days would remove approximately 80% of adsorbed material during a week of standing, providing a repeatable 80% of maximum activity after each week's cycle. This slow decay rate would release heat at an undetectable rate. Applying a rule-of-thumb extrapolation of rate from an assumed 190°C down to 20°C by doubling the rate for each 10°C rise in temperature and assuming a half-life of 10 sec at 190°C, gives an estimate of the half-life of the weathered hopcalite to be approximately 48 hours, or 2 days. This value is consistent with the example assumed above. This investigation examined the possibility of gradual recovery of adsorptive capacity by a slow oxidation process and, indirectly, the permanence of the electron-beam activation of hopcalite.

2.0 EXPERIMENTAL

A set of experiments was designed to test whether our sample of SJAFB's vacuum-irradiated hopcalite was in fact able to regenerate by an oxidation mechanism that is very slow compared to adsorption from the vapor phase. We assembled a test apparatus (Figure 4) that allowed us to confine a measured charge of either toluene or butanone (MEK) and a standard amount of recovered catalyst in mutual isolation. This equipment also permitted quantification of the vapor concentration, and then introduction of the catalyst from the reservoir into the chamber with the vapor. This permitted subsequent measurement of the gas-phase concentrations of the solvent remaining and of carbon dioxide, CO_2, generated after an arbitrary interval of as long as two weeks. To compensate for leakage, a nominally identical vessel was charged with only the same solvent and analyzed in parallel as a control.

Vapor concentration was determined from a sample collected for 10 minutes through a septum. A solid-phase microextraction (SPME) tool (7-μm fiber diameter; Supelco, Bellefonte, Pennsylvania) was used and the concentration measured by direct thermal desorption into the inlet of a gas chromatograph (Hewlett–Packard 5890 Series II). The HP 5890 was fitted with a 30-m-by-0.25-mm (ID) capillary column coated with a 1-μm film of DB-5 (Supelco, Bellefonte, Pennsylvania) and a flame ionization detector (FID). After introduction of the charged SPME, the injection port was maintained at 270 °C. The column temperature was programmed to hold at 40 °C for 5 min to ensure complete desorption into the head of the column. The SPME was subsequently withdrawn and the oven temperature was increased by 10 °C/min to a final value of 160 °C. MEK and toluene were detected at 6.5 and 10.8 min, respectively. Extreme deviations from linearity occur at concentrations of approximately 30,000 ppmv due to detector and gas phase saturation, but the analytical
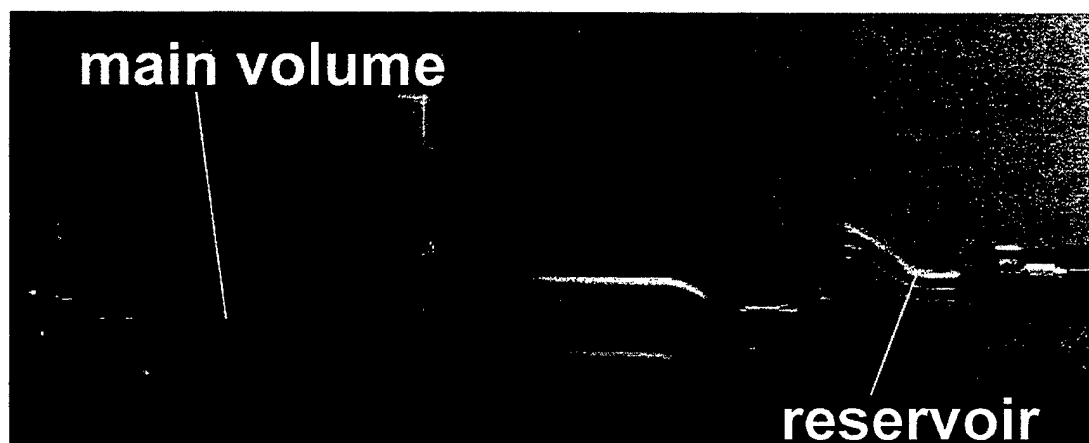

Figure 4. Glass air-sampling tube. Toluene was injected into the main volume through the Mininert™ valve at the center of the tube. The hopcalite was allowed to enter from the reservoir through the stem valve after the toluene evaporated.

response is linear within the concentration range used in this study. A typical calibration curve is displayed as Figure 5.
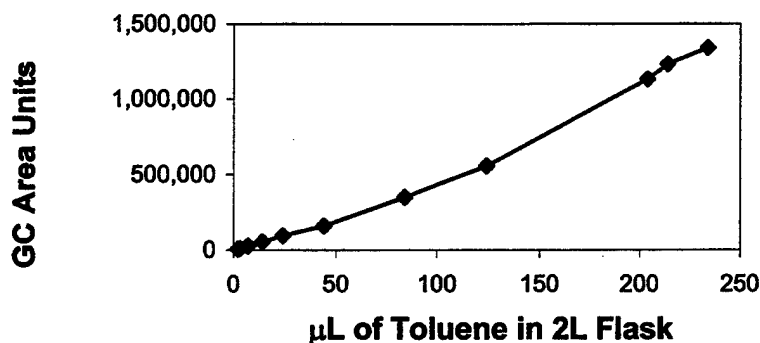

Figure 5. Calibration data for GC/FID

Samples for analysis of CO_2 from oxidation of toluene were collected through the septum into a gas-tight syringe and injected onto a Hewlett–Packard 5851 Series II gas chromatograph fitted with a similar 1% DB-5 column and a Hewlett–Packard 5970 mass-sensitive detector (MSD). The MSD measured CO_2 directly as ion current at m/z 44. The two-point calibration procedure used air (0.03% CO_2) and a commercial standard (Scotty's 237, Scott Specialty Gases, Plumsteadville, Pennsylvania) containing 7.0% CO_2.

Incubations of toluene and MEK were conducted at room temperature (the laboratory HVAC system maintained 24 °C). Following initial evaluation of results, a second set of incubations of MEK at 38 °C was performed. This elevated temperature represented a manned paint booth workspace that was nearly 10°C above the upper temperature tolerance limit. For each incubation one or two individual pellet(s) of recovered hopcalite were weighed and heated to 200°C for 2 hours before introduction into the closed neck of a thoroughly flushed incubation vessel and isolation behind the closed Teflon™ valve. Each pellet weighed approximately 100 mg and the mass of pellet was selected to provide adsorption capacity estimated to be the same as the amount of solvent to be added. No catalyst was introduced into the leakage control, which was prepared at the same time. Into each vessel (125-mL and 500-mL cells were used) 10 μL (to one hopcalite pellet) or 20 μL (to two pellets) of solvent was injected, providing 0.3–0.9 of the saturated vapor concentration in each vessel. Air in each vessel contained more than a stoichiometric equivalent of oxygen for complete combustion of the solvent.

After approximately 30 minutes equilibration was assumed and an initial vapor sample was drawn with the SPME and analyzed. Preliminary experiments suggested that driven motion caused no significant enhancement of evaporation and mixing, and that light did not measurably enhance reaction rates. Therefore, uncovered vessels were clamped in place for the duration of each experimental exercise.

At $t = 0$ for the experiment the valve isolating the hopcalite was opened and the vessel was tipped to drop the pellet(s) into the body of the incubation vessel. Typically two catalyst tests were run concurrently with each control, and the vessel selected for the control was changed from run to run. During the next 30 minutes several vapor samples were drawn and analyzed from each vessel in turn, and the time of each sampling event was noted to map the rate of adsorption of vapor onto the hopcalite pellet. Then vapor samples were drawn and analyzed at intervals of several days for arbitrary lengths of time. Experiments with toluene included a final vapor sample and collection of a second sample for CO_2 analysis. Most experiments were terminated at this step, and the CO_2 analysis was not performed for MEK.

After collection of the final samples for one specific experiment that ran for 39 days, the valve was opened, the vessel tipped to return the hopcalite pellet(s) to the isolation pocket, and then the valve was closed. At this point, the vessel was flushed with air and recharged with the same volume of toluene as originally delivered. After approximately 30 minutes the vapor concentration was measured, the valve was reopened to reintroduce the hopcalite. After 30 additional minutes of exposure of hopcalite to the MEK, another vapor sample was taken and used to determine residual adsorption capacity.

3.0 RESULTS AND DISCUSSION

A summary of results is provided below, and a detailed presentation of the toluene and MEK results is reported elsewhere[18,19]. Figure 6 displays typical toluene behavior. It also shows the results from the reintroduction experiment, in which no evidence of recovered capacity was observed. The experiments with toluene consistently showed rapid adsorption for approximately 30 minutes, presumably tailing toward an asymptote that was not discernable within the time resolution of the data. After the initial measurements, slope calculations produced adsorption rate values similar to those for the corresponding untreated controls.
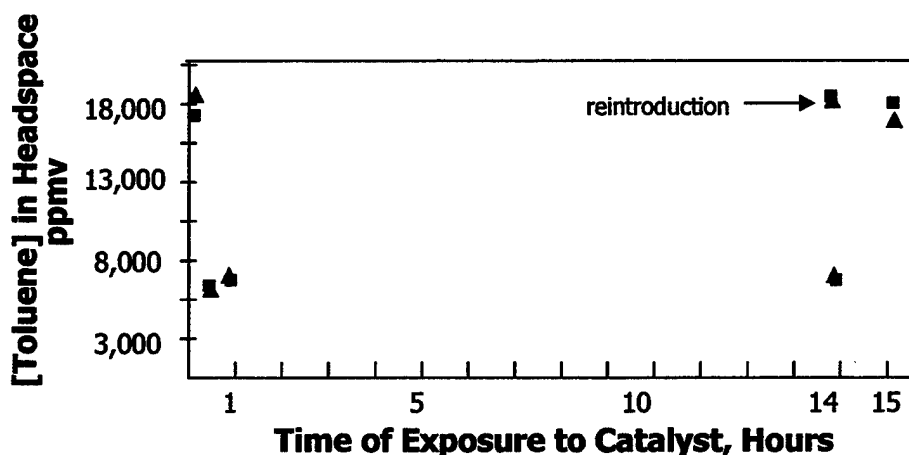

Figure 6. Uncorrected plot of concentration vs time. After equilibration of 10 μL of toluene injected into a 125-mL vessel at 24°C, a freshly regenerated sample of recovered hopcalite (120mg) was introduced into the reactor volume on day 14.

To correct for the effect of leakage, a measured/control ratio was developed. The data were presented as the ratio of the experimental value to the corresponding control value at each time measured. Because the data were relatively noisy, a composite plot of the entire data set was developed on a common grid by normalizing this measured/control ratio observed at 24 hours in all experiments to a relative value of 1. Inspection of Figure 7 suggests a near-horizontal straight-line fit and linear regression analysis of the plotted data revealed a 95% confidence interval for the value of the slope between −0.021 and +0.048. CO_2 concentrations ranged from 0.5 to 2 times atmospheric background. The average measured CO_2 concentration approached the background value for the bottled air used during the experiments.

MEK is considerably more reactive toward oxidation than toluene. To amplify reaction processes possibly concealed by the anticipated strong adsorption to the hopcalite surface, the experimental design was altered to include runs at a temperature 14 degrees higher than the 24°C typical of manned painting processes. For these elevated temperature runs, only the region of data that could exhibit observable oxidation kinetics during the exposure time was plotted.
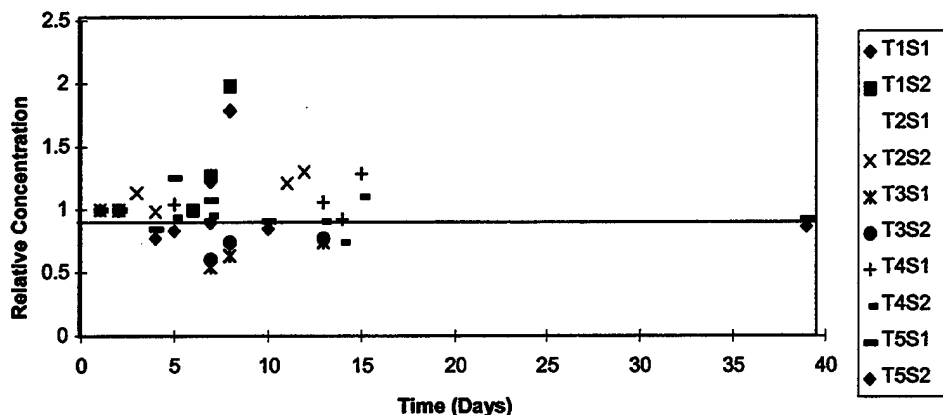
10

Figure 7. Relative concentration of toluene in the headspace as a function of time during experimental runs at 24°C. Data are normalized to concentration after day 1.

The plots in Figures 8 and 9 show normalized MEK measurements at each temperature using the same normalization procedure developed for the toluene data. In Figure 8, there appears to be a slight trend toward decay in concentration with time; however, at 38 °C the trend in Figure 9 appears to be toward a slight increase in concentration with time. From these results, one can confidently conclude that adsorptive capacity of the hopcalite is not gradually recovered by any mechanism operating at temperatures of interest in applications involving ventilation air in manned spaces.
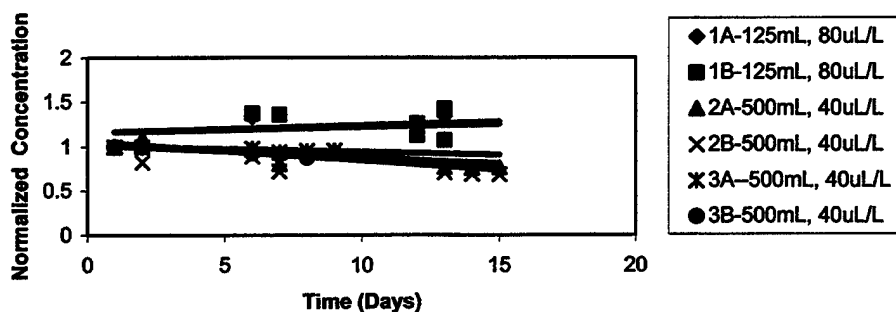

Figure 8. Relative concentration of MEK in the headspace as a function of time during experimental runs at 24°C. Data are normalized as in Figure 7.
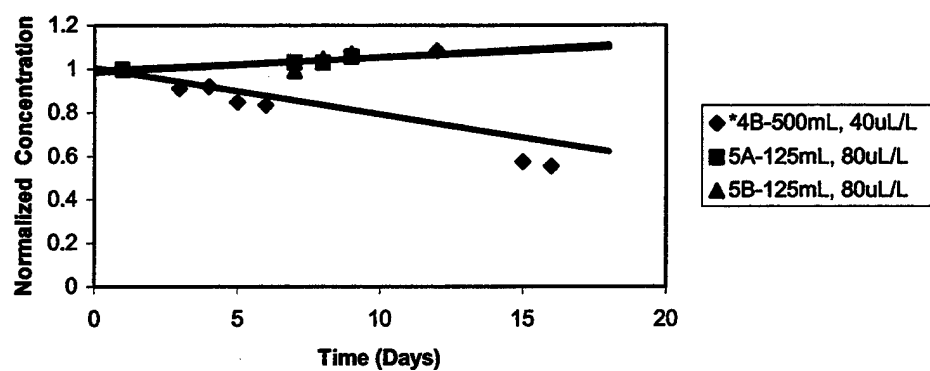
11

Figure 9. Relative concentration of MEK in the headspace as a function of time during experimental runs at 38°C. Data are normalized as in Figure 7.

REFERENCES

1. Wander, Joseph D., Adams, Brian S., Gibbs, Stephen T., and Williston, Christopher A. (2001) *Recirculating Ventilation System in an Integrated Maintenance Hangar Supporting B-1B and KC-135 Aircraft*, AFRL-ML-TY-TP-2001-0031, Air Force Research Laboratory, Tyndall AFB, Florida.

2. Carlton, G.N., and Flynn, M.R. (1997) "A Model to Estimate Worker Exposure to Spray Paint Mists," *Ann. Occup. Environ. Hygiene*, **12**, 555–561.

3. Carpenter, D.R., and Poitrast, B.J. (1990) *Occupational Health Assessment, Building 2280, Tinker AFB OK*, AFOEHL Report 90-094CA00188EDC, AF Occupational and Environmental Health Laboratory, Brooks AFB, Texas.

4. NFPA 33, *Standard for Spray Application Using Combustible or Flammable Materials*, 1995 Edition (and earlier editions), National Fire Protection Association, Quincy, Mass. Section 5.2

5. 29 CFR 1910.94(c)(6)(ii).

6. Plummer, J.E. (1997) 8 April Letter to Munsell, E., Deputy Assistant Secretary of the Navy, Environment and Safety, http://131.158.51.236/osha_cd/osha/OshDoc/INTERP~2/I1AB2C~1.HTM

7. 29 CFR 1910.1000.

8. NFPA 33, *Standard for Spray Application Using Combustible or Flammable Materials*, 1995 Edition (and earlier editions), National Fire Protection Association, Quincy, Mass. Sections 5.5, 5.5.1, 5.5.2.

9. Wander, J.D. (2002) "Cost-Effective Ventilation for Large Spray-Painting Operations," *Metal Finishing*, **100**[*3*], 23–27.

10. LaPuma, P.T., and Bolch, W.E. (1999) "The Impact of Recirculating Industrial Air on Aircraft Painting Operations," *Applied Occup. Environ. Hygiene*, **14**[10], 682–690.

11. Hughes, S., Ayer, J., and Sutay, R. (1994) *Demonstration of Split-Flow Ventilation and Recirculation as Flow-Reduction Methods in an Air Force Paint Spray Booth*, AL/EQ-TR-1993-0002 / EPA/600/R-94/214a, Armstrong Laboratory, Tyndall AFB, Florida.

12. http://nersp.nerdc.ufl.edu/~lapuma/index.html

13. 40 CFR 63.745(b).

14. Zerbonia, R. A., Brockmann, C. M., Peterson, P.R., and Housley, D. (2000) "Carbon Bed Fires and the Use of Carbon Canisters for Air Emissions Control on Fixed-Roof Tanks." Proceedings Air & Waste Management Association 93rd Annual Meeting & Exhibition, Salt Lake City, Utah, paper #256, A&WMA, Pittsburgh, Pennsylvania.

15. Lamb, A.B., Bray, W.C., Frazer, J.C.W. (1920) "The Removal of Carbon Monoxide from Air." *J. Ind. Eng. Chem.*, **12**, 213–221.

16. Ramsey, G. (1994) "Low Temperature Catalyst," presentation at Seymour Johnson AFB, N.C., 10 February; summarized in Princiotta, F., Letter to Klimet, A., Air Quality Section, NC Dept. of Environmental Health & Natural Resources, 26 April 1994

17. Henley, M., Mahone, W., Mayfield, H.(1994) "Moldan Trap Material Evaluation," reprinted as Appendix A in refs. 18 and 19.

18. Crowe, R.K. (1998) *An Experimental Search for Slow Reactions of Toluene Adsorbed on Hopcalite at Room Temperature*, Thesis, Florida State University, Tallahassee, Florida.

19. Scott, J.L. (2001) *Adsorption and Catalyzed Oxidation of Methyl Ethyl Ketone on Activated Hopcalite at 24 and 38 Degree Temperatures*, Thesis, Florida State University, Tallahassee, Florida.

20. Allred, V.D., Hill, G.R. (1952) *The Chemical Characterization of Oxidation Catalysts: Hopcalite*, Technical Report Number I, ONR project number NR057 192.

21. Petkovska, M., Tondeur, D., Grevillot, G., Granger, J., Mitrovic, M. (1991) "Temperature-swing gas separation with electrothermal desorption step," *Separation Science and Technology*, **26**, 425–444.

22. Cha, C.Y., Provens, T., Wright, G., and Wander, J. (2002) *Microwave Treatment of Hypergolic Fuel and Oxidizer Vapors*, AFRL-ML-TY-TP-2002-4520, Air Force Research Laboratory, Tyndall AFB, Florida

APPENDIX

The generic process illustrated in the Seymour Johnson AFB facility is modeled below. The development identifies the lowest measured rate of oxidation (by a catalyst, plasma, or other device) of adsorbed VOCs. For illustration purposes, the limiting oxidation rate constant, k, for the Seymour Johnson facility is calculated for two percent recirculation rates using the derived equations for k. The catalytic system uses a steady-state recirculation model and assumes pseudo-first order catalytic oxidation of the VOCs in a uniform catalytic bed directly behind the filter.

The model assumes a rectangular paint booth with air exiting the wall opposite to the inflow air as seen in Figure 3 (page 5). All air exiting the paint booth passes through a particulate filter that has the dimension of the exit wall. A bed of oxidative catalyst is placed directly behind the filter and also has the dimensions of the exit wall. The exhaust air is divided and r is defined as the percent of the exhaust flow that is released to the atmosphere and $(1 - r)$ is recycled back to the front of the paint booth. To maintain a constant airflow in the paint booth ($Q = 5000$ ft^3/s), clean air is added to the front end of the booth and mixed with the recirculated fraction of exhaust through the filter. VOCs are introduced via the paint guns at a rate of $G = 64.8 \times 10^{-4}$ lb·VOC/sec.

Analysis of the concentration of the VOCs in the cross sectional area of the booth beyond the spray guns (G) and before the filter bed results in the following mass balance of VOCs.

$$\Sigma \text{mass rates in} = \Sigma \text{mass rates out}$$

mass VOCs in the recirculated portion of the exhaust		mass VOC introduced with the paint gun		mass VOCs entering the exhaust filter (leaving the paint booth)
	$+$		$=$	

$$(1-r)QC_{exh,recat'} + G = QC_{ss,recat'}$$

Assuming pseudo-first-order (for which $C = C_0 e^{-kt}$) destruction of VOCs in the catalyst bed,

$$C_{exh,recat'} = C_{ss,recat} e^{-kt}$$

Substuting $C_{ss,recat'}$ in the mass balance and solving for $C_{ss,recat'}$,

$$(1-r)\,QC_{ss,recat'}\,e^{-kt} + G = QC_{ss,recat'}$$
$$C_{ss,recat'} = G/Q[1/(1-(1+r)e^{-kt})]$$

Introducing known information,

Room Dimensions: height (h) = 20 ft; width (w) = 50 ft; length (l) = 80 ft
Air Flow Velocity = 100 ft/min

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Air Flow Rate: Sectional Area x Air Flow Velocity (ft/s) = Q = 100,000 ft^3/m
Spray Gun Rate: G = 64.8 x 10^{-4} lb·VOC/sec (constant)
Percent airflow exhausted: r = 20% and r = 1%.

Further assuming that

the temperature in the system is constant;
the exit exhaust concentration is at steady state; and
instantaneous adsorption occurs prior to the catalytic oxidation of the VOC,

Defining the following,

$C_{exh,recat'}$ (lb/ft^3) = VOC concentration leaving the catalyst bed
$C_{ss,rcat'}$ (lb/ft^3) = steady-state VOC concentration in the paint booth beyond the
paint spray gun
k (sec^{-1}) = catalyst first-order rate constant
t (sec) = contact time (time to flow through the catalyst bed)

And assuming a uniform 1-inch thick catalyst bed with a constant flow rate gives a
contact time of 0.05 sec.

$$t = [1 \text{ in}] \times [1 \text{ ft/12 in}] / [100 \text{ ft/min}] \times [1 \text{ min/60 sec}]$$
$$t = 0.05 \text{ sec}$$

Substituting the steady-state concentration into the design equation:

0.19 gun rate ≥ exhaust rate
$0.19\ G = rQC_{exh,recat'}$
$0.19\ G = rQC_{ss,recat'}\ e^{-kt}$
$0.19\ G = [rQe^{-kt}]G/\{Q[1 - (1+r)e^{-kt}]\}$

Rearranging and simplifying:

$0.19 = [re^{-kt}]/[1 - (1+r)e^{-kt}]$
$0.19[1 - (1+r)e^{-kt}] = re^{-kt}$
$0.19 - 0.19e^{-kt} - 0.19re^{-kt} = re^{-kt}$
$0.19 = (0.81r + 0.19)e^{-kt} + 0.19e^{-kt}$
$e^{-kt} = 0.19/(0.81r + 0.19)$
$-kt = \ln[0.19/(0.81r+0.19)]$
$k = -\ln[0.19/(0.81r + 0.19)]/t$

The smallest rate constant (k) that will support the described control system is calculated
for two values of the percent of air flow exhausted, r = 20% and r = 1% for a constant-
temperature system and a 0.05-second exposure time of the VOCs to the catalyst using a
uniform 1-inch deep catalyst bed.

for $r = 20\%$ and $t = 0.05$ sec:

$k = -\ln[0.19/(0.81*0.20 + 0.19)]/0.05$ sec

$k_{0.20} = \underline{\textbf{12.33 sec}^{-1}}$

for $r = 1.0\%$ and $t = 0.05$ sec:

$k = -\ln[0.19/(0.81*0.01 + 0.19)/0.05$ sec

$k_{0.01} = \underline{\textbf{0.083 sec}^{-1}}$

These values of the rate constant show the minimum acceptable values of the rate constant of an instantaneous oxidation catalyst for a compliant facility when incorporating partial recirculation of the bulk airflow.

The extent of removal can also be a factor for optimization in a cost-as-an-independent-variable calculation. The recirculation ratio, r, could, in principle, be increased until $C_{ss,recat}$ (and the concentrations actually encountered) exceeds either the Permissible Exposure Limit (PEL; 29 CFR 1910.1000) or the Lower Explosive Limit (LEL; 29 CFR190.94). However, the exposure risk to workers increases as r increases and imposes a limitation on the ambient concentration of airborne air toxic materials.